

Revealing aromatics formation in combustion using experimental and modeling methods

by

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Technical Summary

Aromatic species have always been important in industry, but even increasingly so in recent years. Besides the large amount of aromatics produced as commodity chemicals, soot formation caused by polycyclic aromatic hydrocarbons (PAH) leads to serious clogging or pollution in the petrochemical industry. Therefore, understanding aromatics formation has been prioritized to improve the efficiency of desired chemical production processes. Advanced experimental techniques and detailed models help us draw a complete picture of aromatic chemistry. This thesis includes a modeling work for rich natural gas combustion where syngas, ethylene (C_2H_4), and acetylene (C_2H_2) are the valuable products, and aromatics are undesired byproducts. Through high-level quantum chemistry calculations performed in literature and trained into Reaction Mechanism Generator (RMG), aromatic chemistry was understood from a theoretical viewpoint and accurately predicted by the model. For example, Hydrogen-Abstraction- C_2H_2 -Addition (HACA) was identified as the leading pathway of naphthalene formation ($C_{10}H_8$, one of the simplest PAHs). To measure and validate critical aromatic kinetics in models, we designed and built a new compact quartz reactor to replace a stainless steel reactor in a unique apparatus combining laser absorbance spectroscopy (LAS) and time-of-flight mass spectrometry (TOF-MS). Reaction networks including phenyl radical (C_6H_5) + C_2H_4 and C_6H_5 + C_2H_2 (reactants of HACA) have been investigated for their kinetics and time-dependent product branching ratios. At various temperatures and pressures, the total rate constants of C_6H_5 + C_2H_4 were measured by LAS and direct product quantification of both networks was reported from TOF-MS measurements. Experimental measurements successfully validated detailed models built from *ab initio* calculations without fitting any kinetics parameters. Furthermore, the importance of HACA in developing three fused-benzene ring species was emphasized, and reactions of naphthyl radicals ($C_{10}H_7$) + C_2H_2 were investigated theoretically along with new pathways connecting networks of 1- $C_{10}H_7$ + C_2H_2 and 2- $C_{10}H_7$ + C_2H_2 . Pressure dependence of kinetics in this dissertation was considered due to the high temperature nature of natural gas combustion; therefore, the pressure effects in a natural gas pilot plant have been studied to apply chemistry learned from calculations or experiments to the real-world chemical industry. Overall, studies in this dissertation successfully investigate fundamental aromatic chemistry through experimental and theoretical approaches and connect them to natural gas combustion for future process development.

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